



Manipulating the Coffee Ring Effect



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Outline

- Introduction
- How and Why do Coffee Rings Form?
- Manipulating Coffee Rings
 - Reversing the Effect
 - Particle Shape and Size
 - Other Factors
- Conclusion

Coffee Ring Effect



- What is the coffee ring effect?
- Why do we care?

VERTEBRATE EVOLUTION
THE FACE OF CHANGE
A jawless fossil – but designed for jaws
PAGE 324



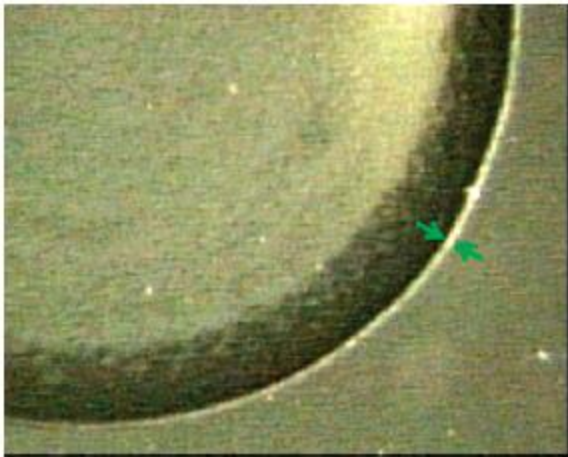
PRIMATES
CANDID CAMERAS
Do chimpanzees have culture?
PAGE 266

WOMEN IN SCIENCE
A FEMALE LEAD
Role models for success in chemistry
PAGE 273

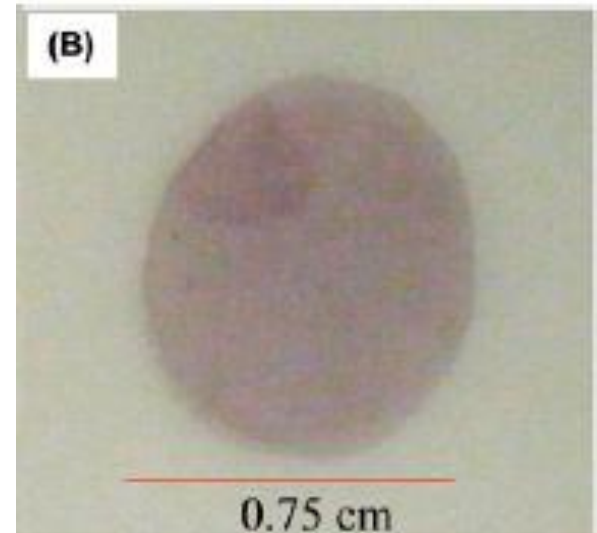
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Vol 476 No 7360

The Two Sides of the Fence

- Enhance the effect



- Minimize the effect



What causes the effect, and how can we manipulate it?

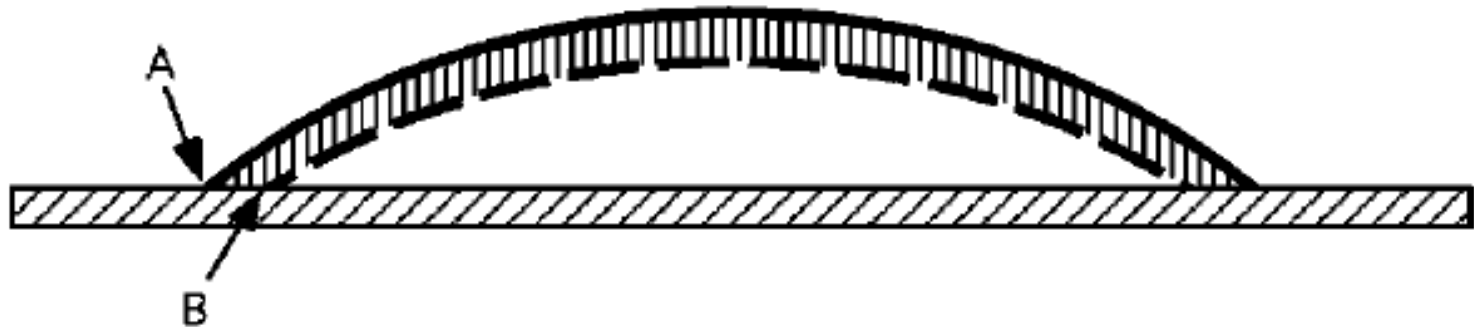
Formation of Coffee Rings

- Why do they form?
- What is required?
 - Contact angle
 - Pinning
 - Evaporation

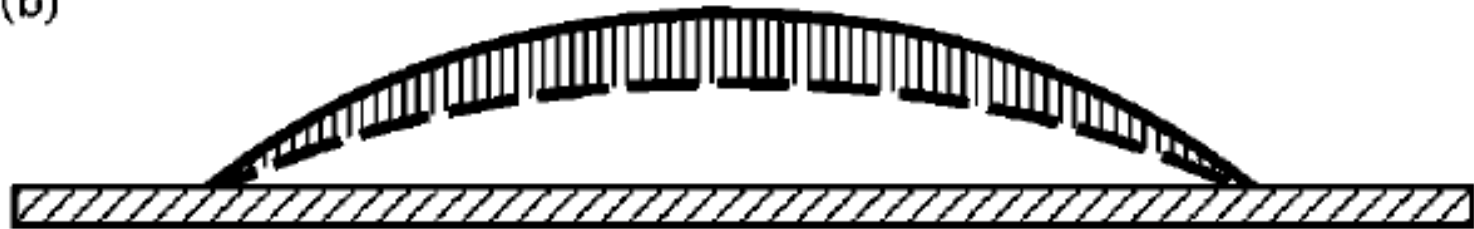


Coffee Rings are a *Geometrical* Effect

(a)



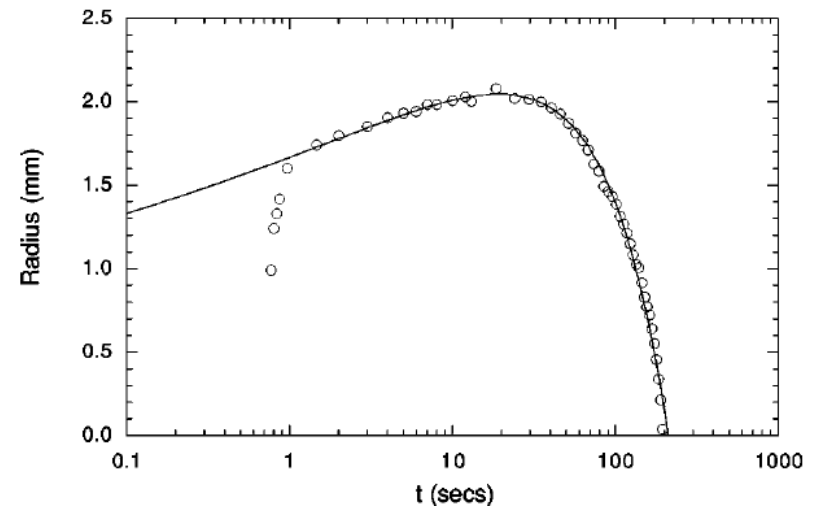
(b)



What Causes the Pinning?

- Surface Irregularities
- Deposited Particles
 - Self-Pinning

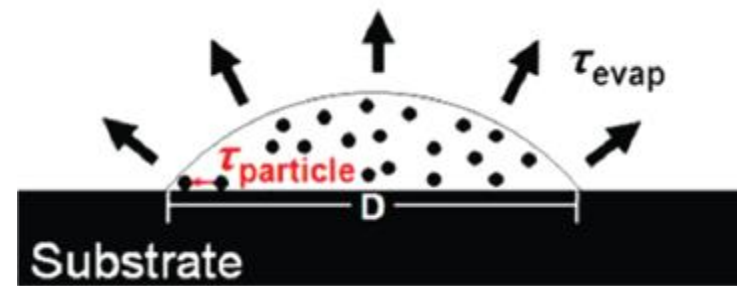
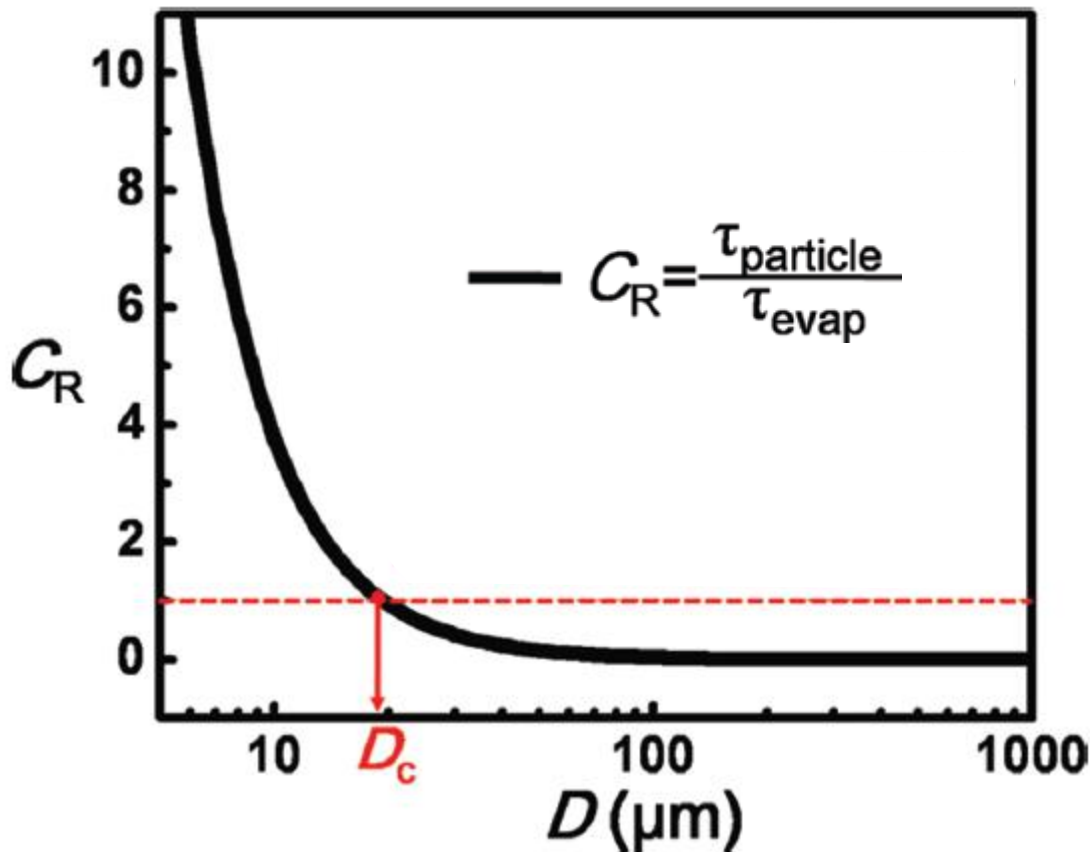
Water Droplet Radius as a Function of Time on an Atomically Flat Mica Surface



Deegan, R.D., et al., "Pattern formation in drying drops," *Phys. Rev. E* **61** (2000).

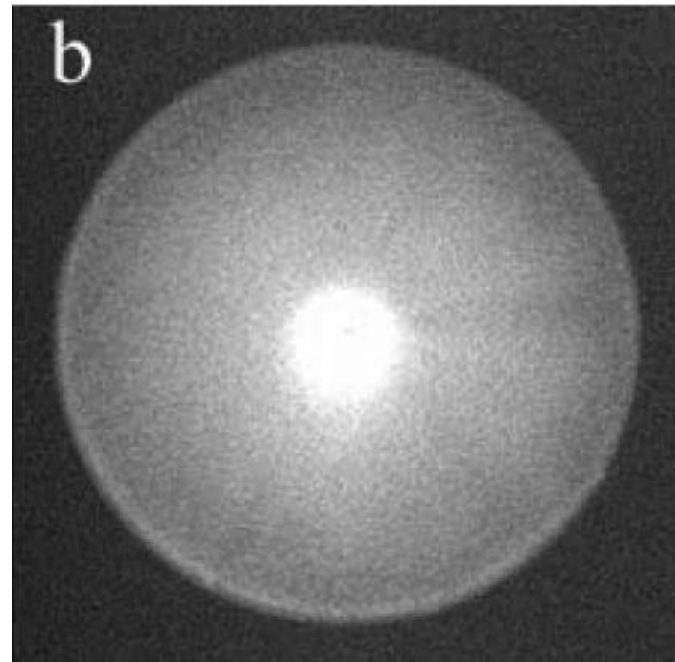
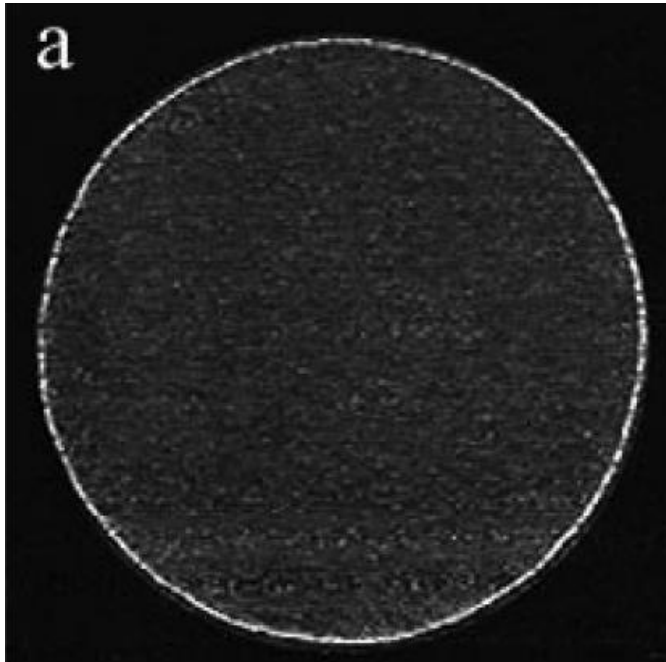
Magdassi, S., et al, "Ring Stain Effect at Room Temperature in Silver Nanoparticles Yields High Electrical Conductivity," *Langmuir* **21** (2005).

Droplet Size Criteria

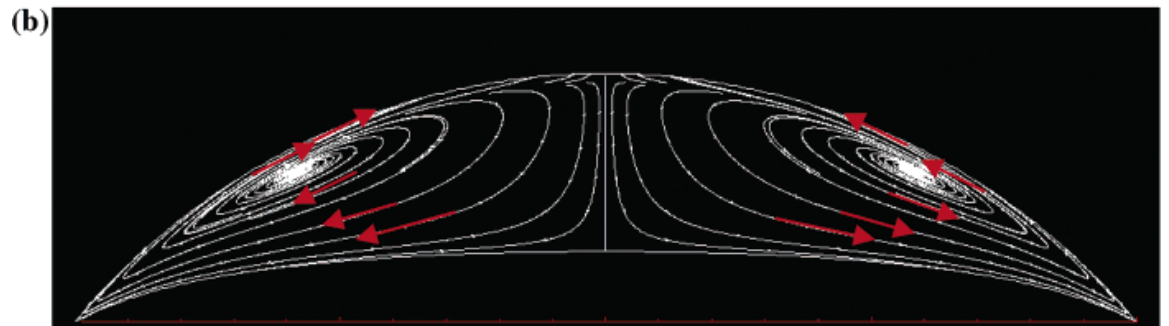
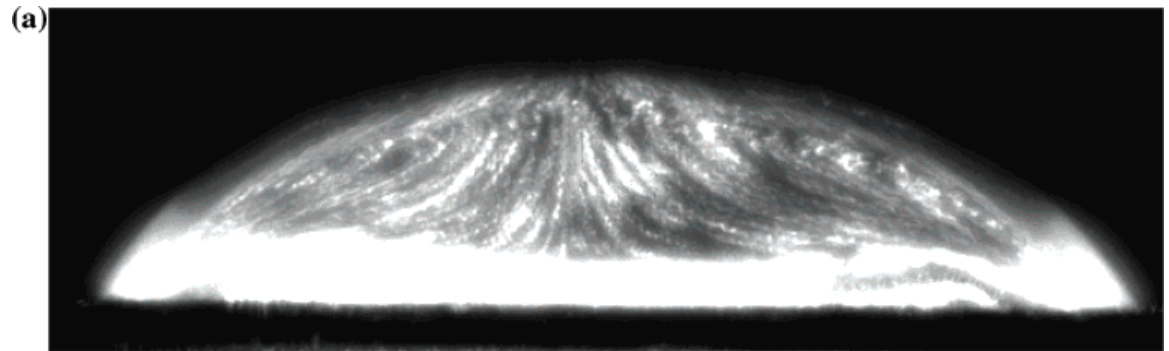
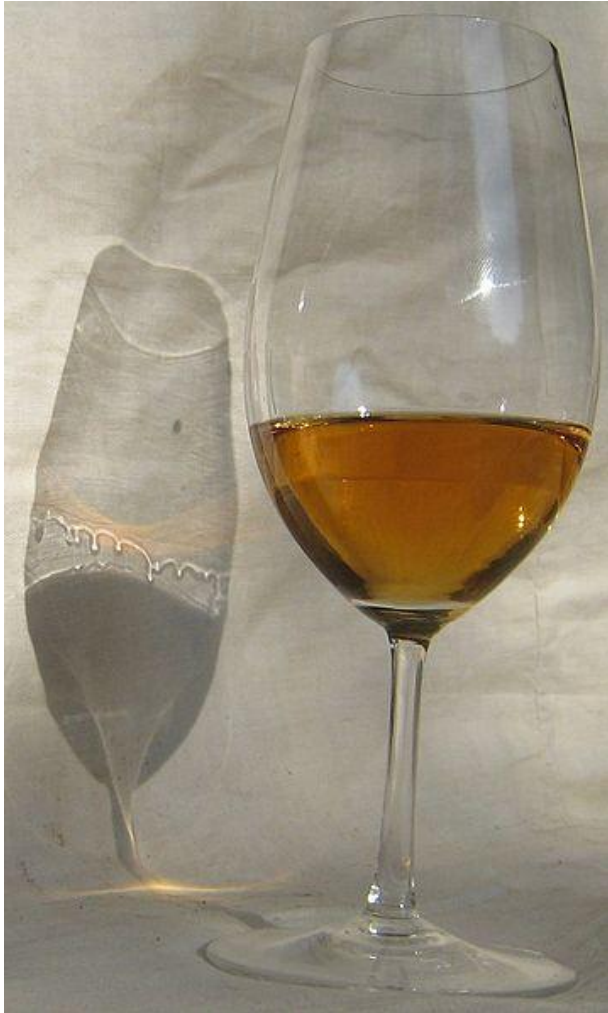


$C_R < 1$ Coffee Ring Formation
 $C_R > 1$ No Coffee Ring

Reversing the Effect



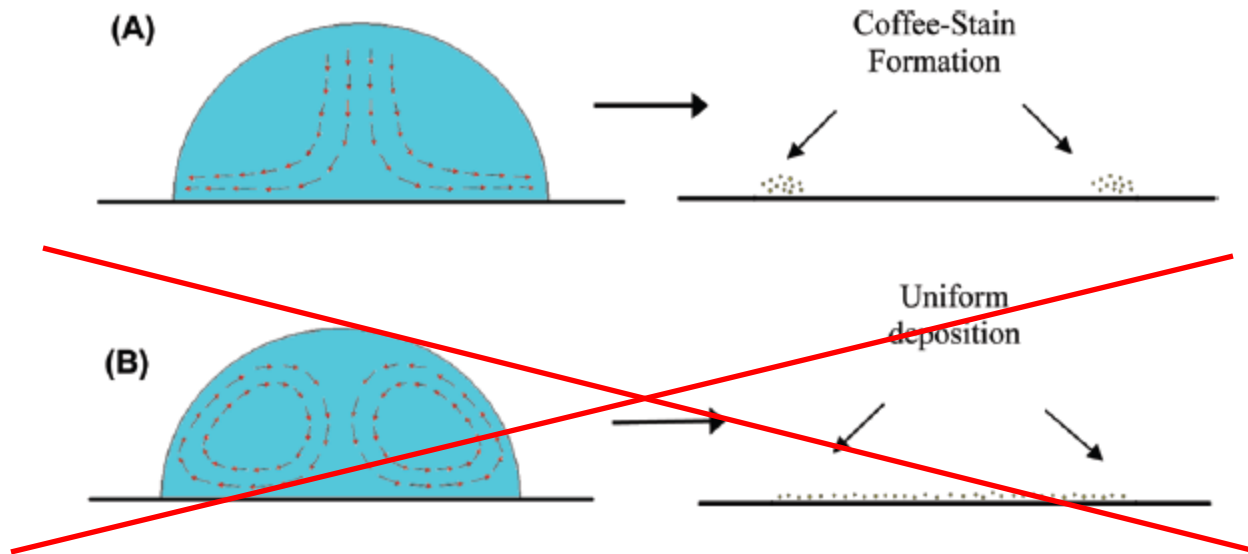
Marangoni Effect



Recirculatory Flows



What's so different about water?



- “The case of water is a long lasting story.”
- Surface contaminants affect water surface tension

Savino, R., et al, “Buoyancy and Marangoni Effects in an Evaporating Drop,” *J. Thermophys. Heat Transfer* **16** (2002).

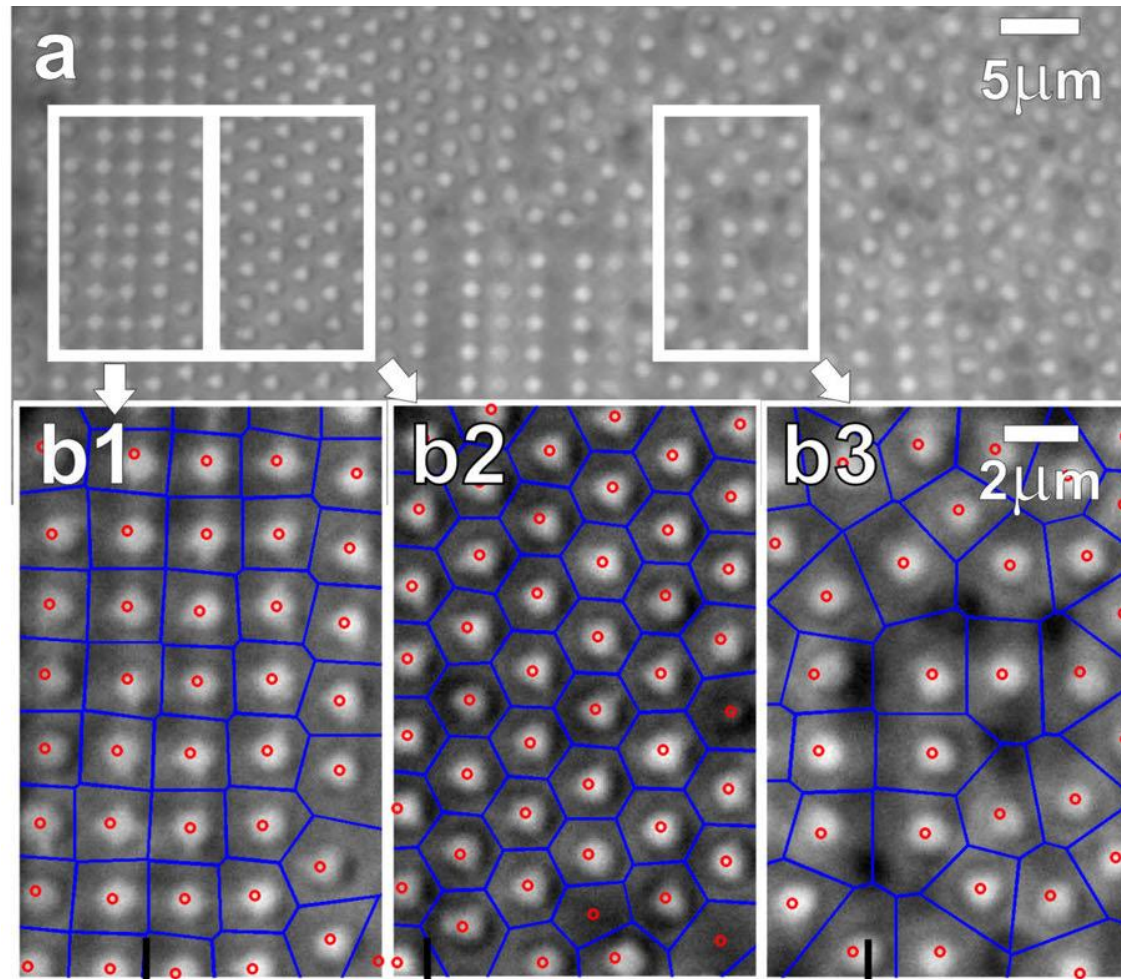
Majumder, M., et al,, “Overcoming the ‘Coffee-Stain’ Effect by Compositional Marangoni-Flow-Assisted Drop-Drying,” *J. Phys. Chem. B*, **116** (2012).

Poulard, C., et al, “Diffusion-driven evaporation of sessile drops,” *J. Phys.: Condens. Matter*, **17** (2005).

And Back to Coffee Ring Formation...

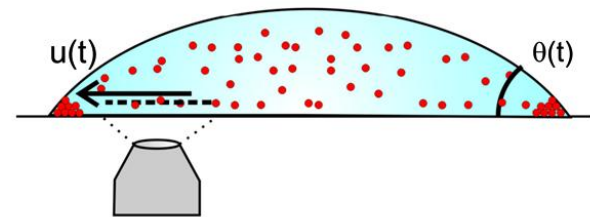
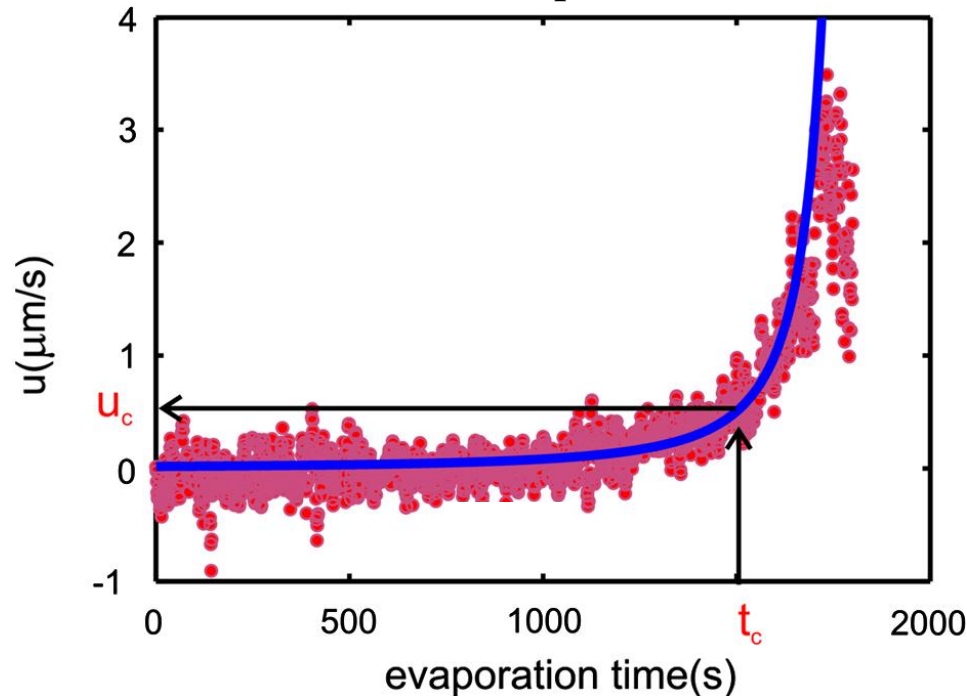
- What is required?
 - Contact angle
 - Pinning
 - Evaporation
 - Minimum Droplet Size
 - Suppression of Marangoni Effect
- How do particles arrange within the ring itself?

Order-to-Disorder Transition



The Rush-Hour or Tetris Analogy

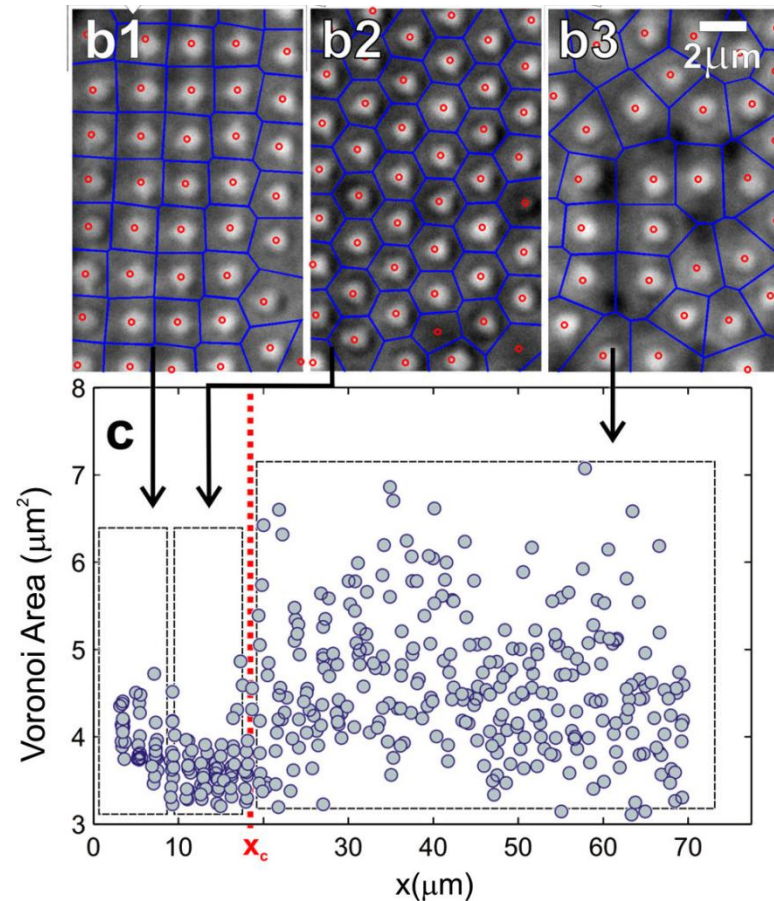
Radial Particle Velocity as a Function of Evaporation Time



$$A(t) \cdot u(t) = \text{Const}$$

This isn't quite the whole story...

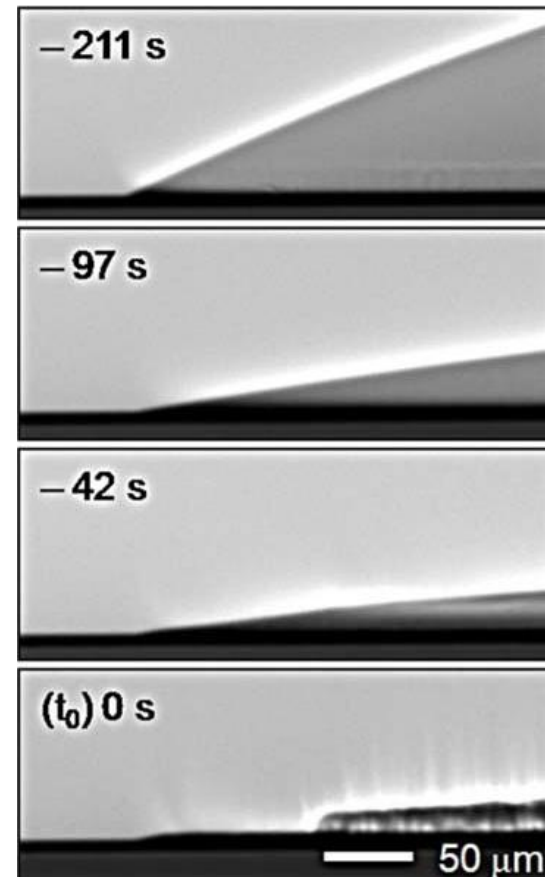
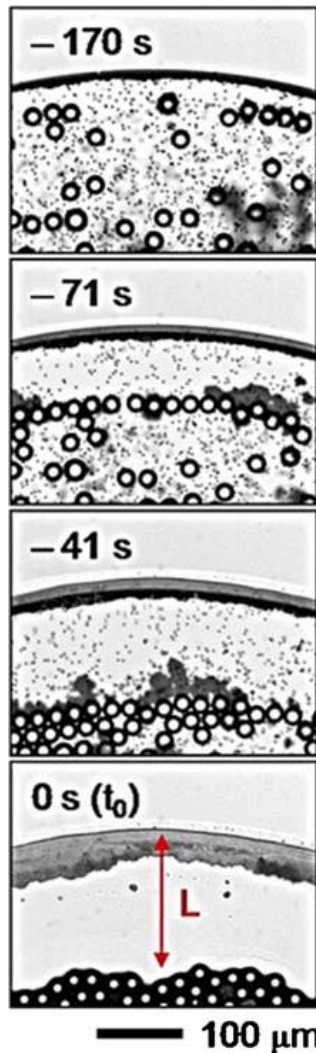
- Voronoi Areas
- Confinement



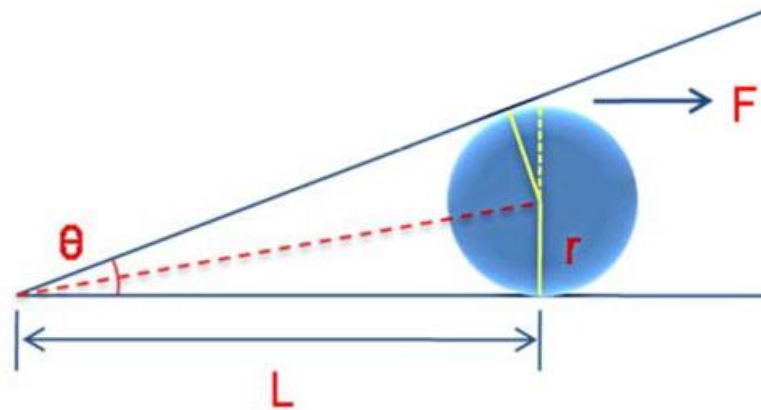
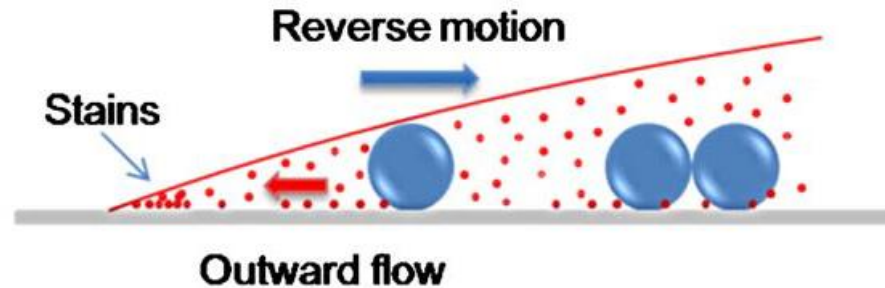
Confinement Effects



So how can we manipulate coffee rings?

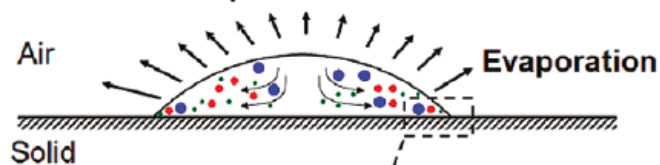


Geometric Constraints

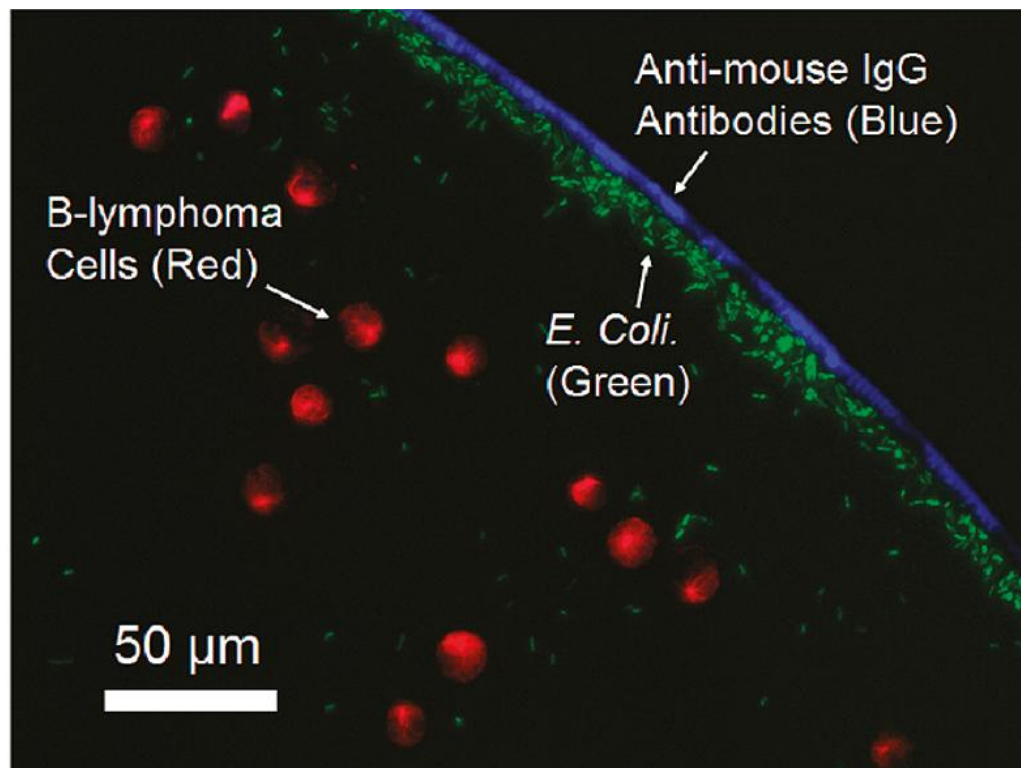
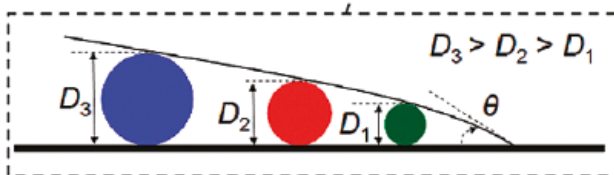


Health Care Application

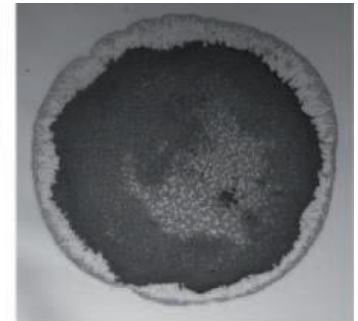
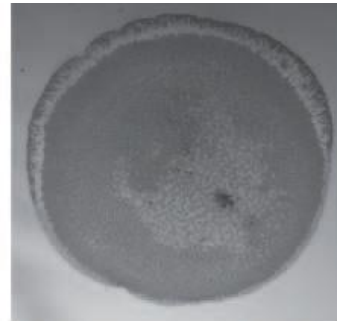
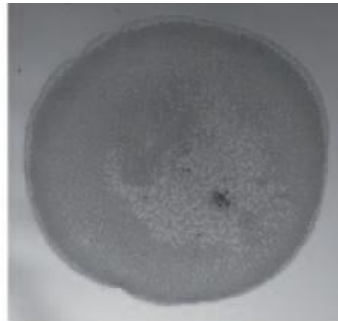
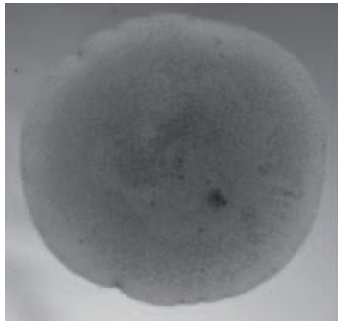
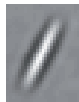
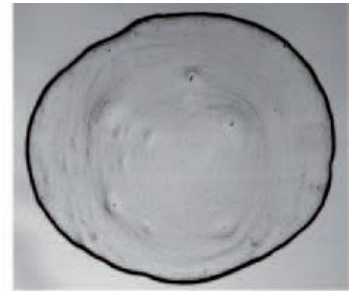
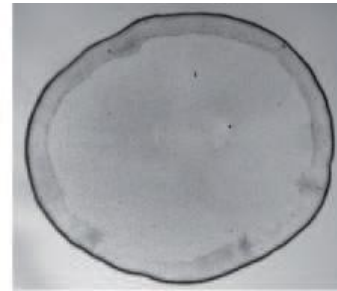
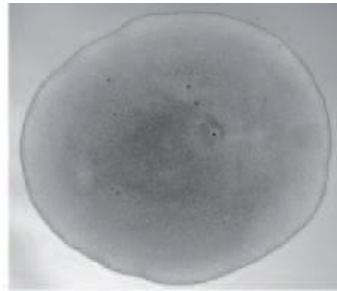
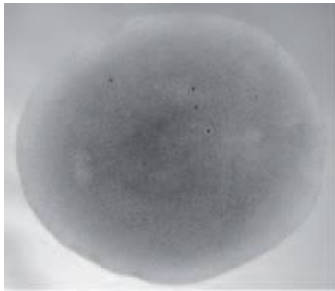
A Colloidal Droplet on a Solid Surface



Near the Contact Line



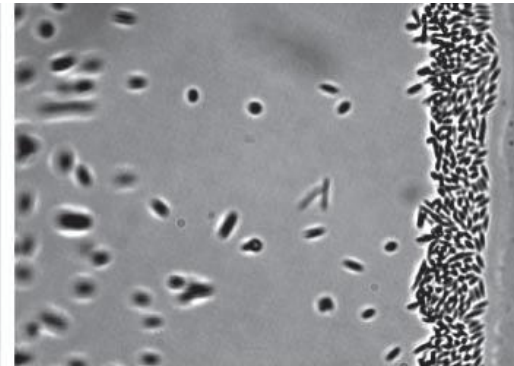
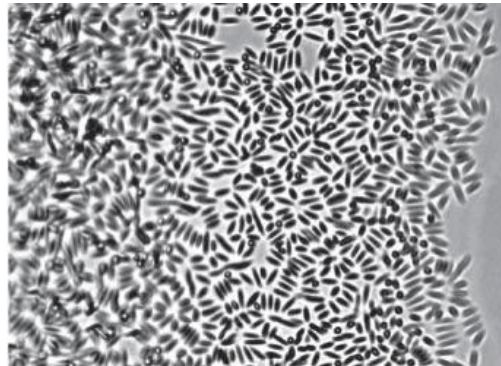
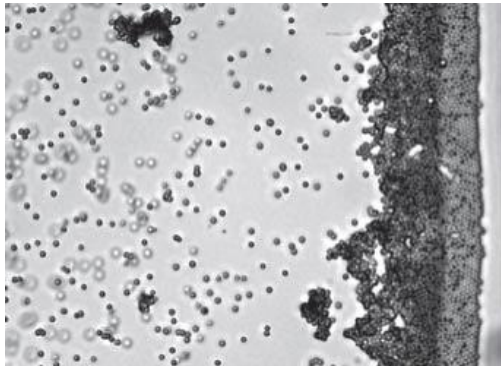
What about the shape of the particles?



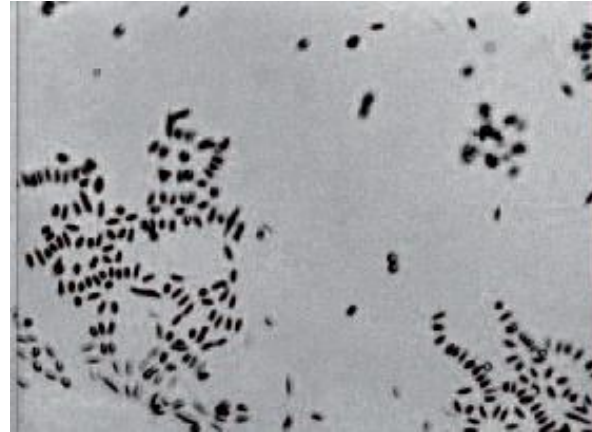
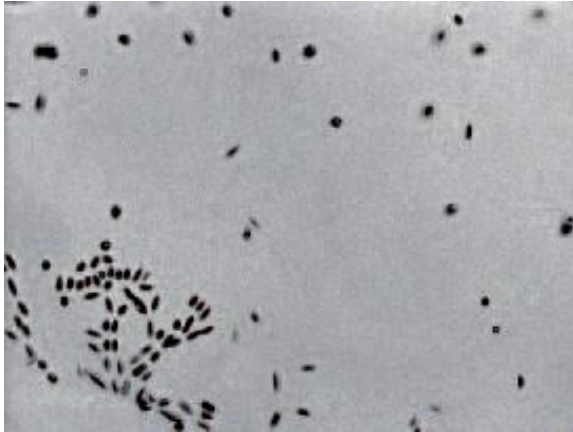
...or is it the shape?



+ surfactant

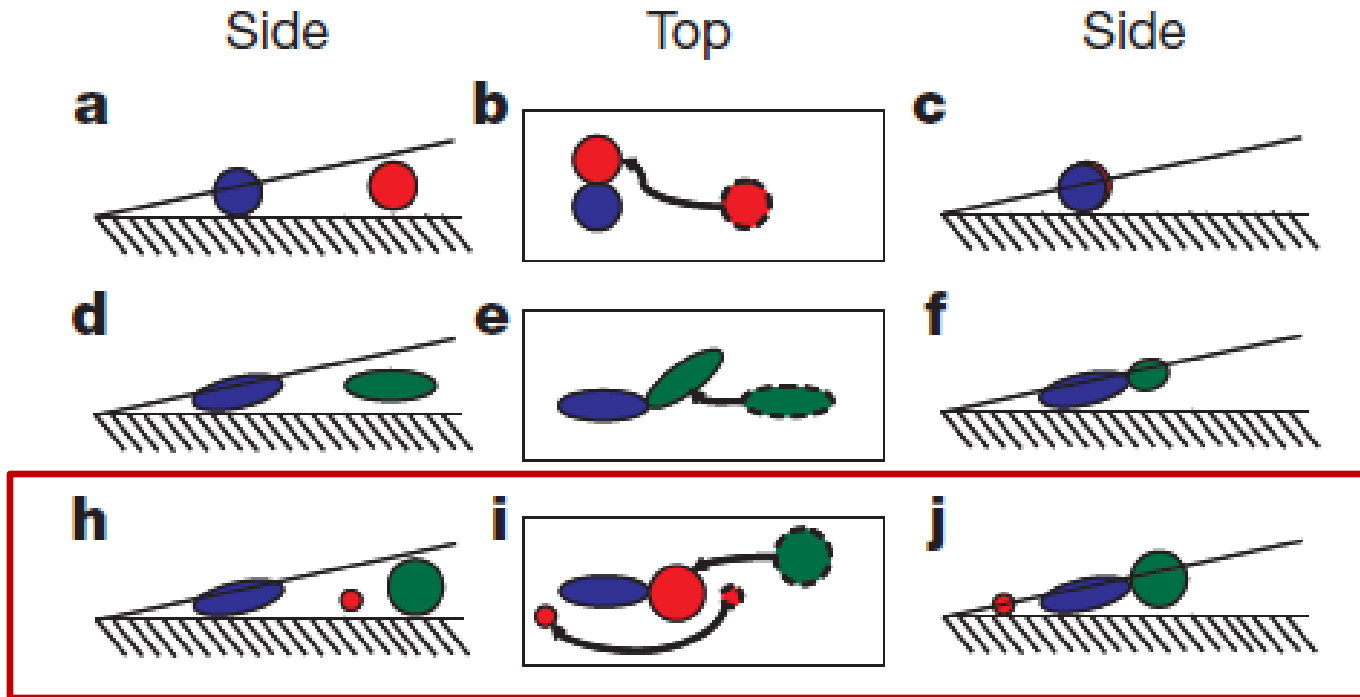


What's actually going on here?

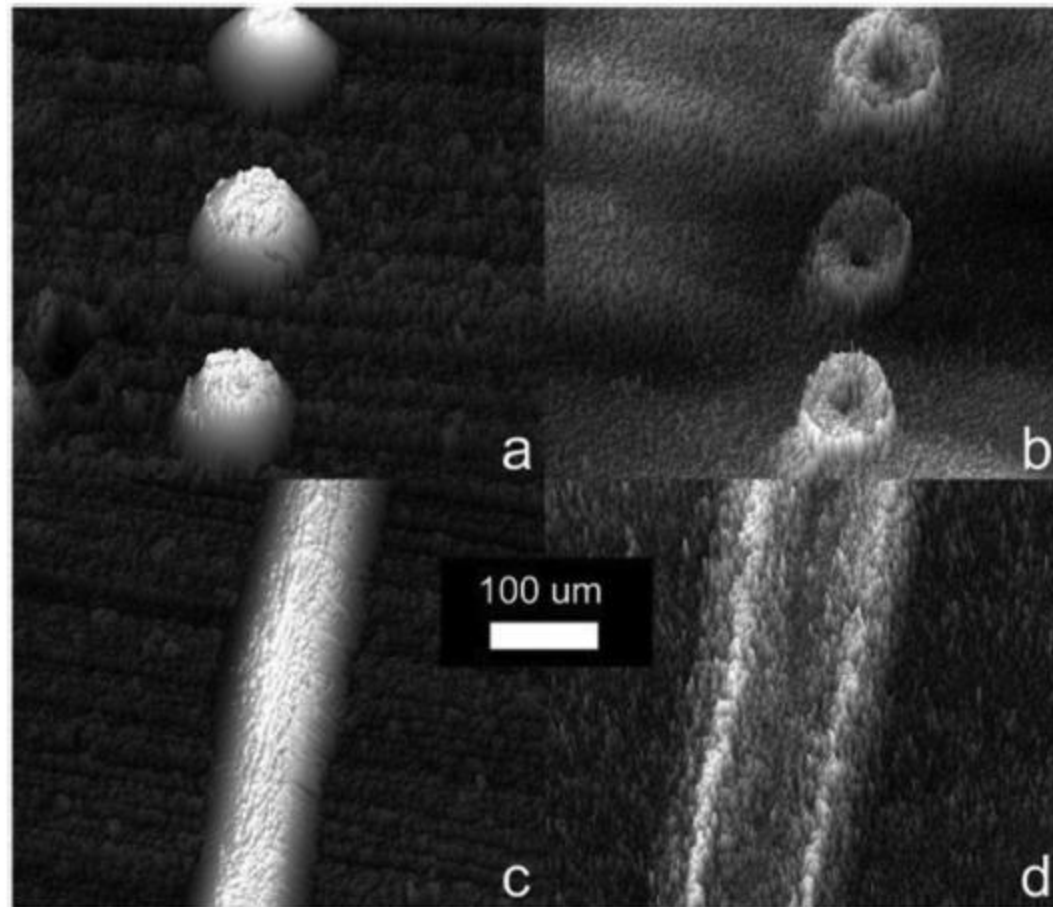


Yunker, P.J., et al, "Suppression of the coffee-ring effect by shape-dependent capillary interactions", *Nature* **476**, (2011).
Park, B.J., and E.M. Furst, "Attractive interactions between colloids at the oil-water interface," *Soft Matter* **7** (2011).
Vella, D., and L. Mahadevan, "The 'Cheerios effect,'" *Am. J. Phys.* **73** (2005).

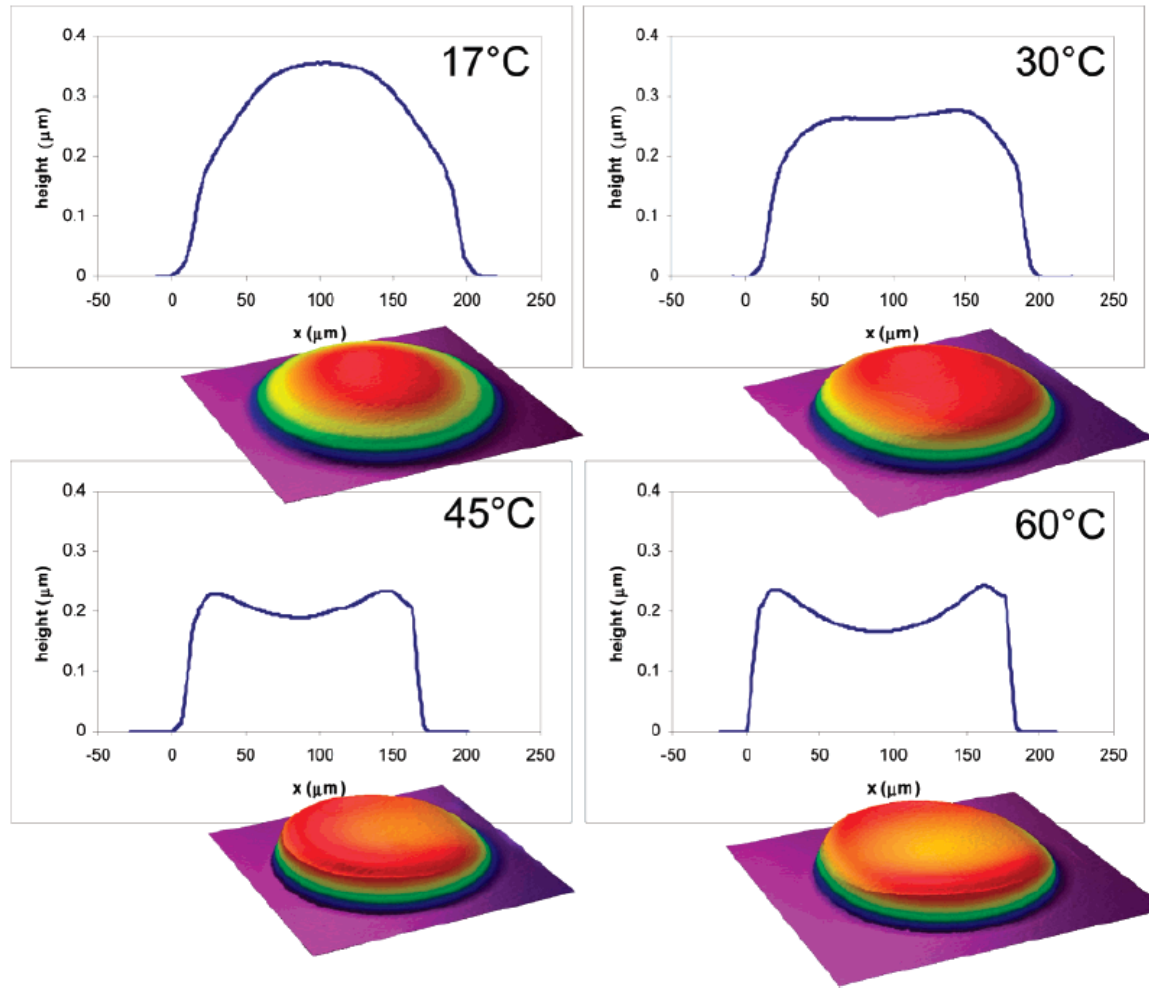
Non-Homogeneous Size/Shape Distribution



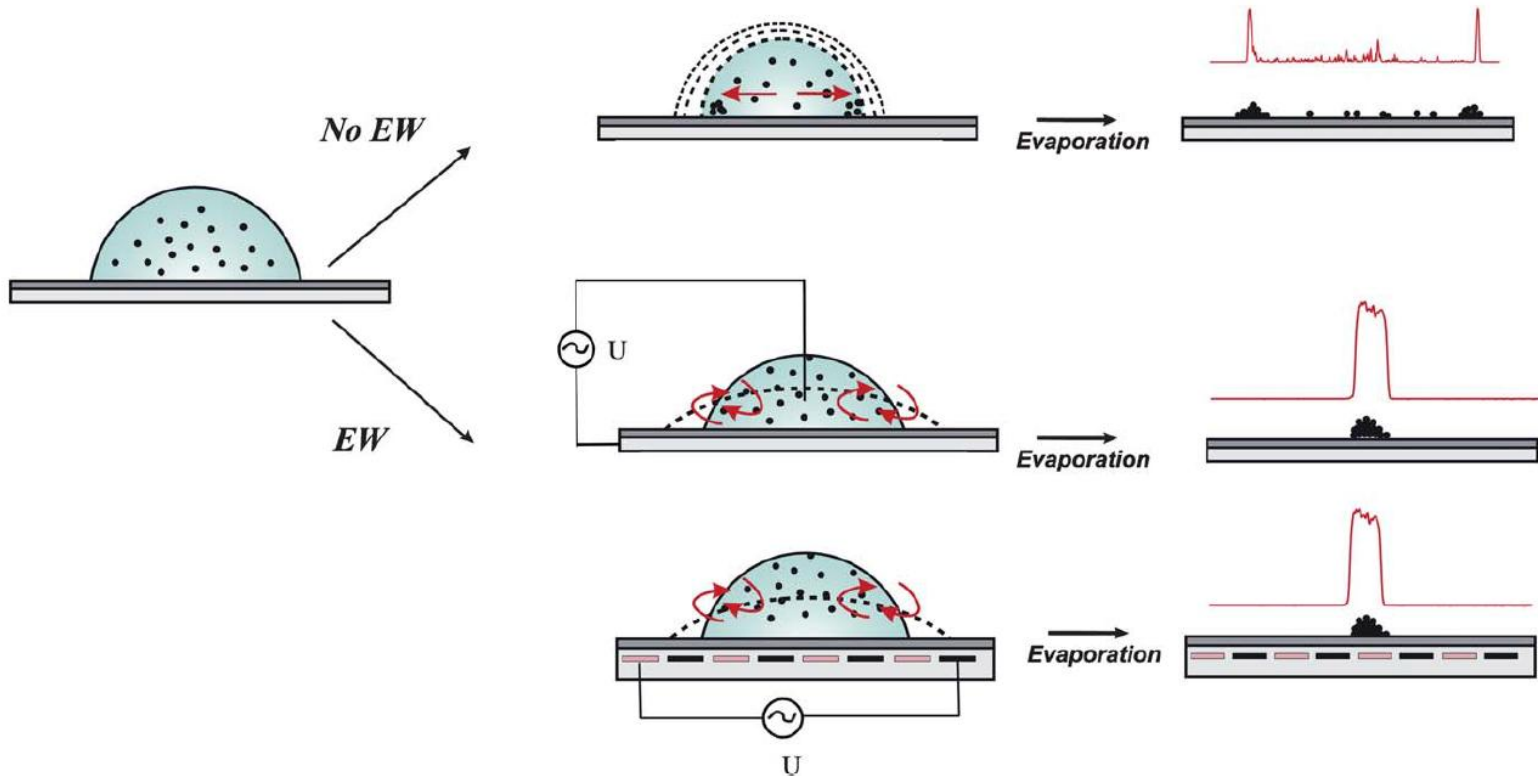
Substrate Composition



Temperature Control



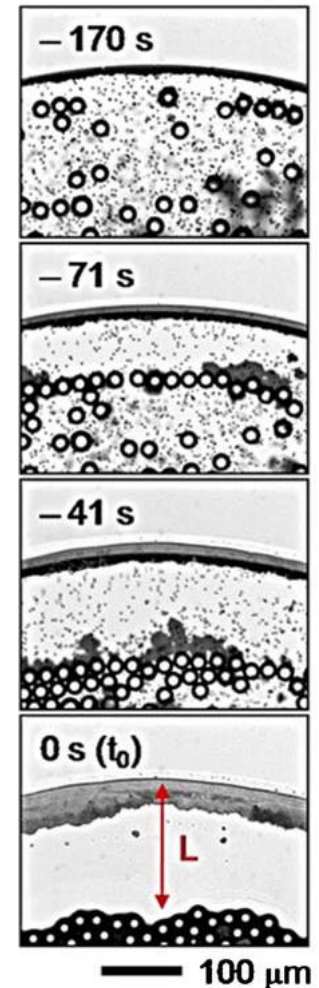
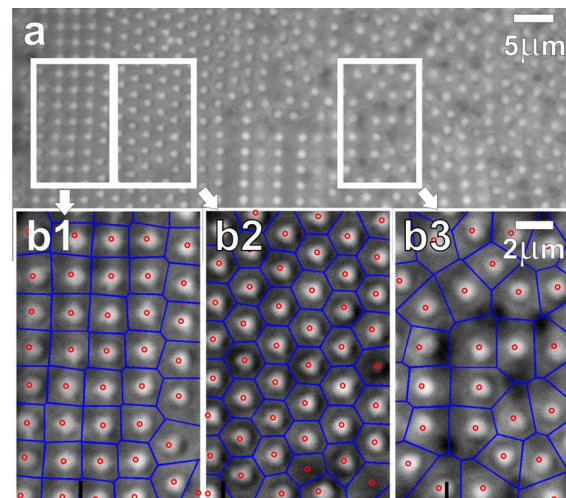
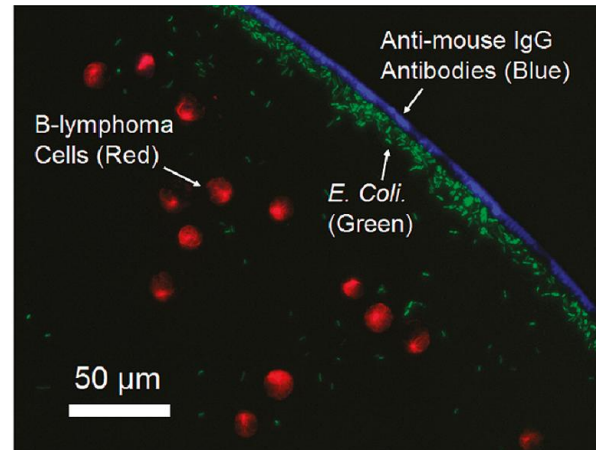
Electrowetting



Conclusion

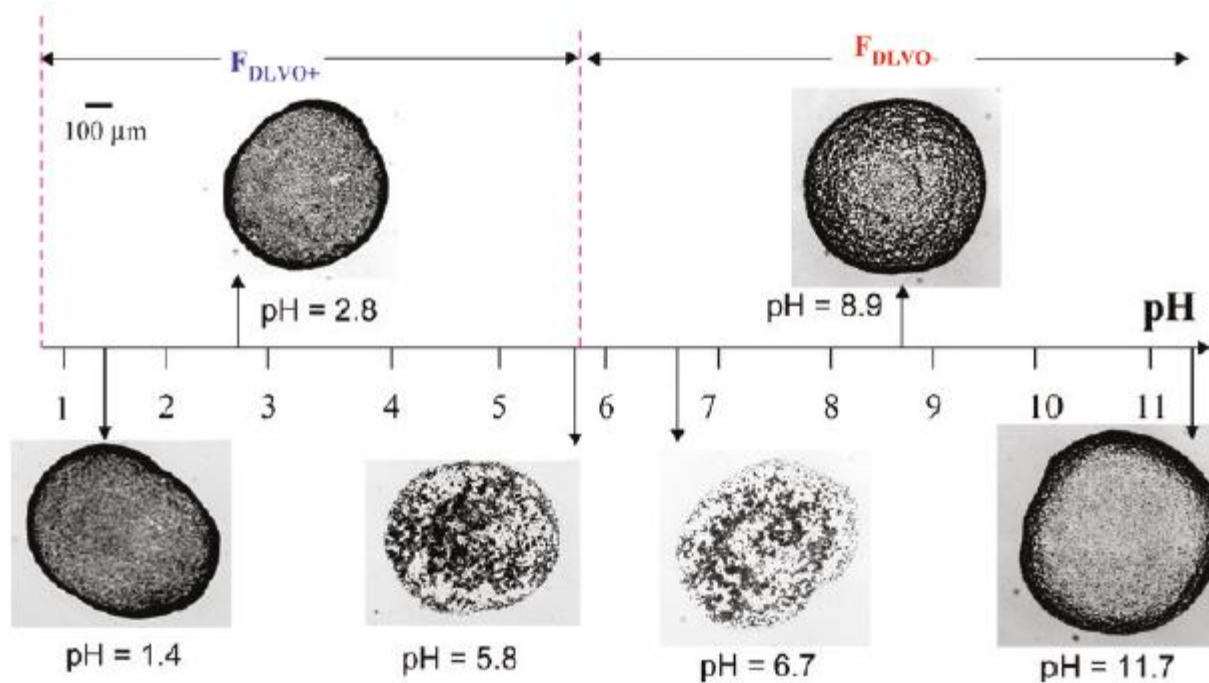
- Surface tension
- Surfactants
- Particle size
- Particle shape
- Solvent
- Evaporation rate
- Applied electric field
- Temperature
- Substrate Porosity
- pH
- Others?

Quantitative
Predictive Model?

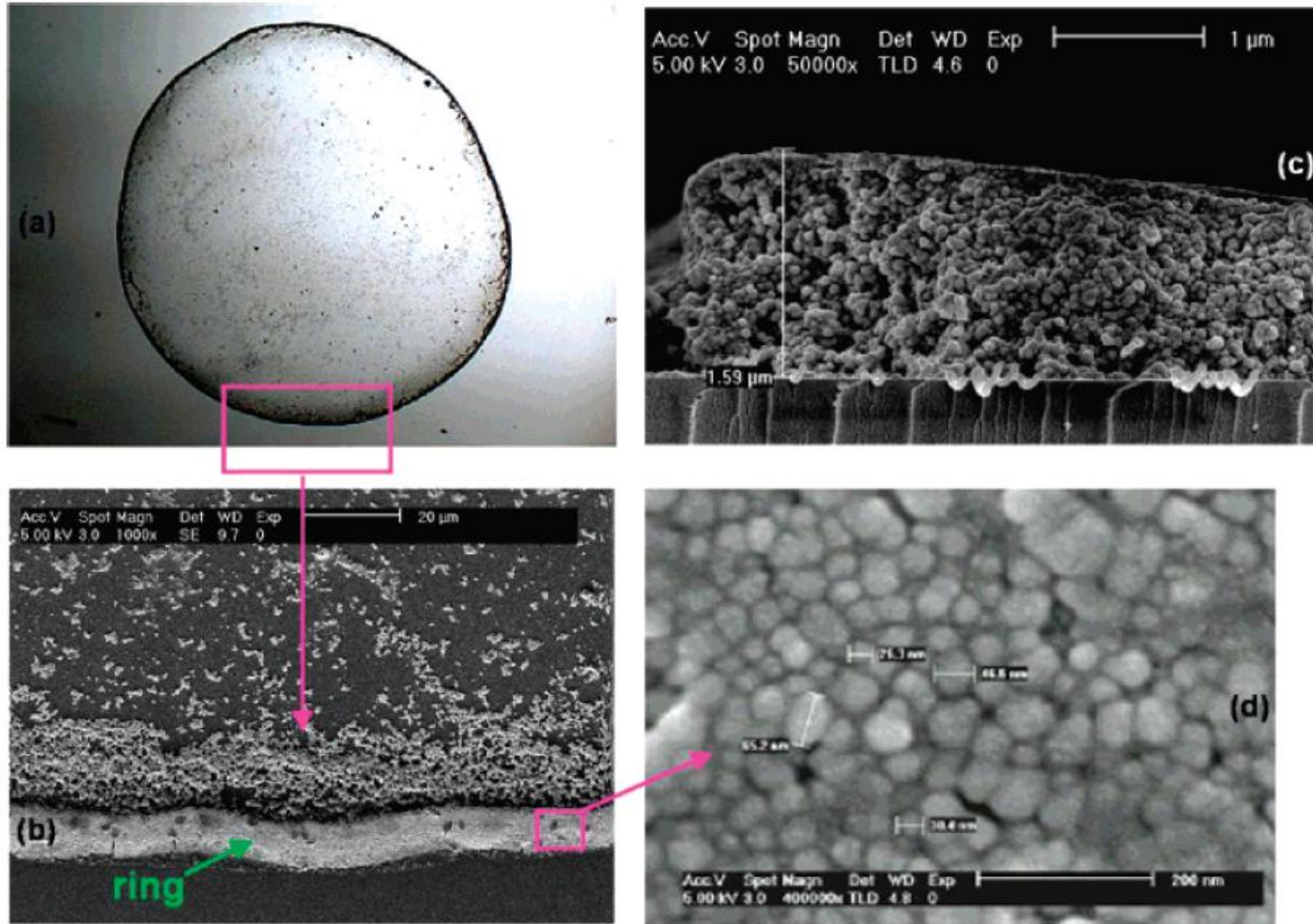


Backup Slides

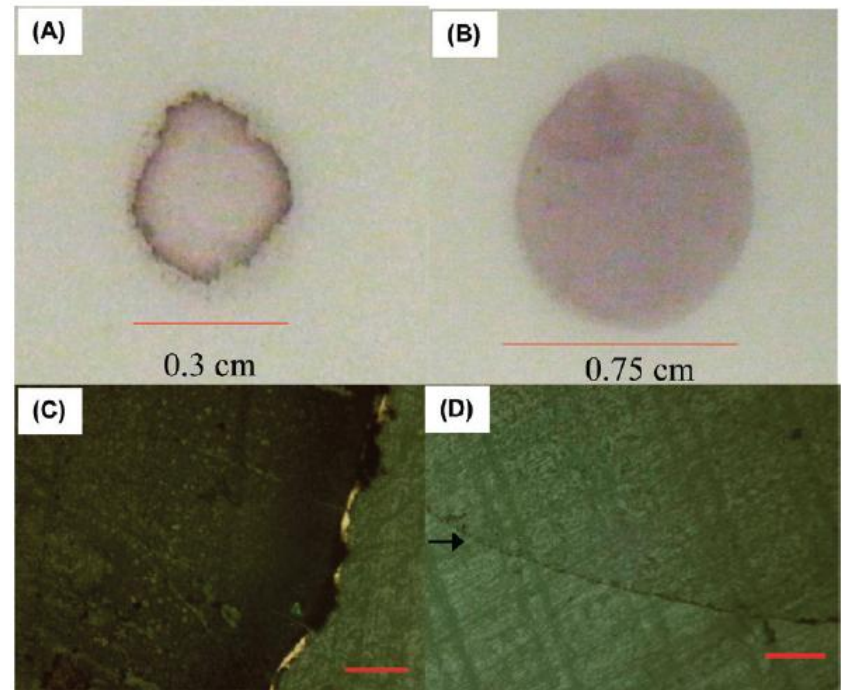
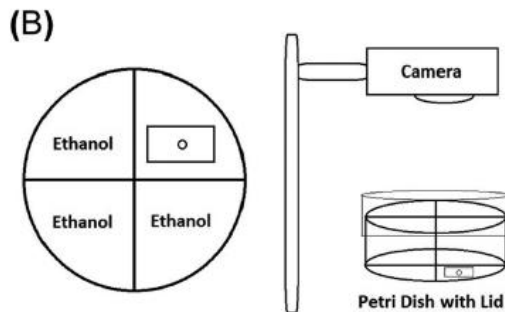
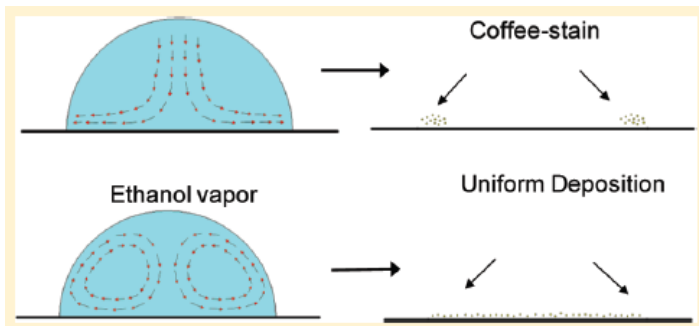
pH Control



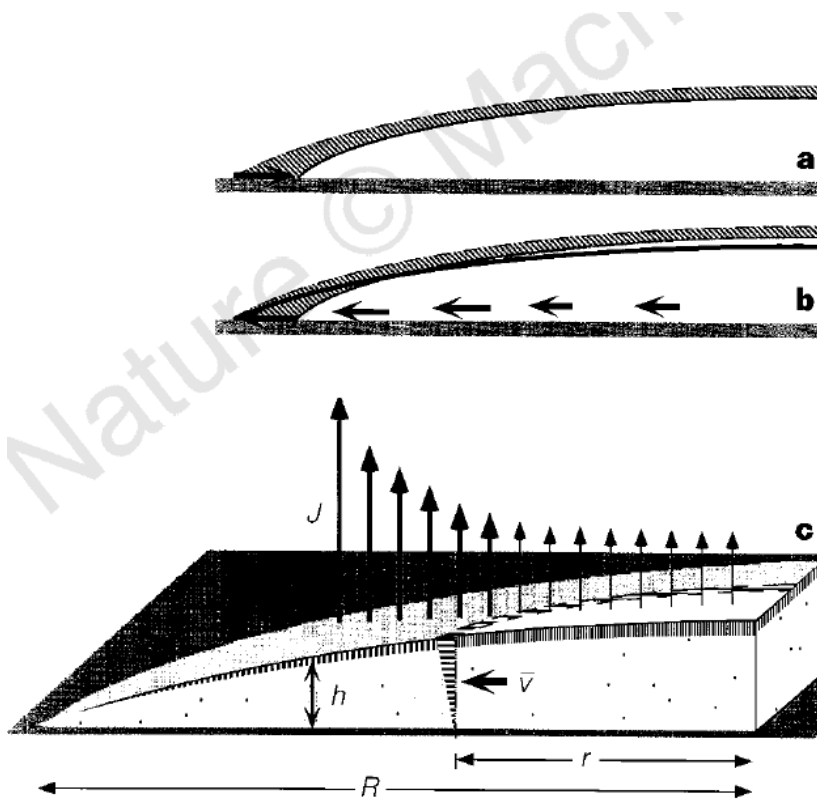
Silver Nanoparticle Rings



Marangoni-Flow-Assisted Drop-Drying



Evaporative Flux

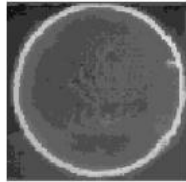


$$J(r) = (R - r)^{-\lambda}$$

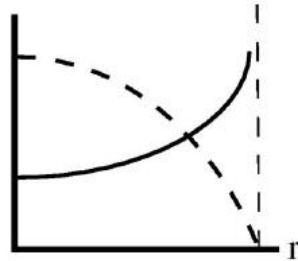
$$\lambda = \frac{\pi - 2\theta_c}{2\pi - 2\theta_c}$$

$$\theta_c \rightarrow 0 \Rightarrow \lambda \rightarrow \frac{1}{2}$$

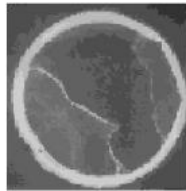
Evaporation Profiles



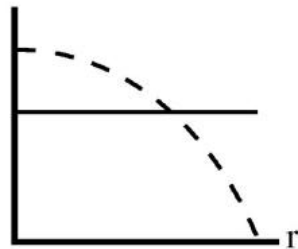
$$\frac{dM}{dt}, J$$



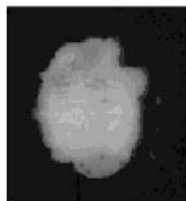
Normal Evaporation



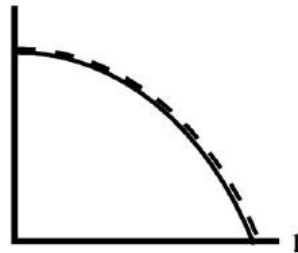
$$\frac{dM}{dt}, J$$



Surrounded by bath of water, water level at base of droplet

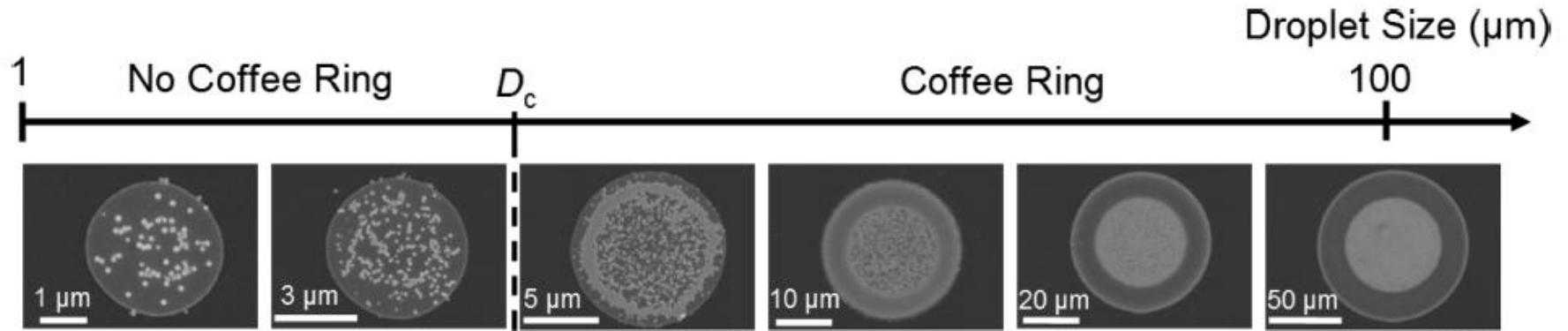


$$\frac{dM}{dt}, J$$



Inside chamber with small hole above droplet center

Minimal Droplet Size



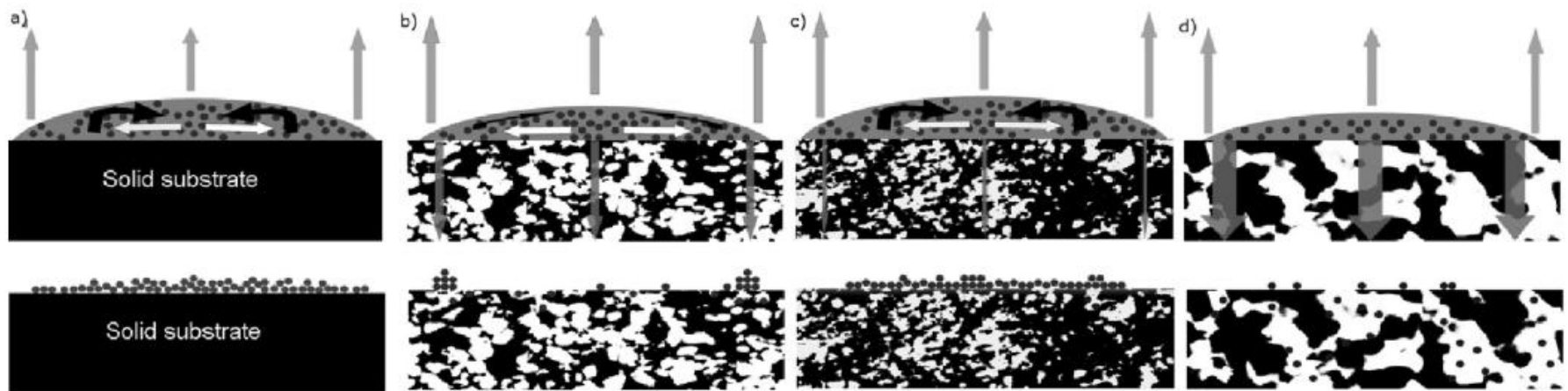
$$C_R = \frac{\tau_{particle}}{\tau_{evap}} \quad \tau_{evap} = \frac{\theta_{initial} - \theta_{receding}}{4K} \pi \left(\frac{D}{2} \right)^2 \quad \tau_{particle} = \frac{\overline{L_m^2}}{2D_p}$$

$$K = \frac{4D_v(c_0 - c_\infty)}{\rho_L}$$

$$L_m = \sqrt[3]{\frac{V_d}{n}}$$

$$D_p = \frac{k_B T}{6\pi\eta r}$$

Substrate Porosity



The Cheerios Effect

